Inexpensive NaX (X = I, Br, Cl) as a halogen donor in the practical
Ag/Cu-mediated decarboxylative halogenation of
aryl carboxylic acids under aerobic conditions
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S1
**General considerations.** The Reagents used for experiments were commercially available and were used as received unless otherwise noted. DMSO were distilled from CaH$_2$ under reduced pressure and stored under nitrogen. All Reactions were performed under dioxygen with the strict exclusion of moisture using Schlenk techniques. Column chromatography was performed on silica gel 300-400 mesh. The yields reported are the isolated yields and the average of two runs. $^1$H, $^{13}$C and $^{19}$F NMR spectra of compounds (1a-14a, 1b-14b and 1c-14c) were recorded at 400, 100 and 377 MHz with CDCl$_3$ as solvent respectively, $^1$H and $^{13}$C NMR spectra of compounds (15 and 16) were recorded at 400 and 100 MHz with d$_6$-DMSO as solvent respectively. All coupling constants ($J$ values) were reported in Hertz (Hz). HRMS were performed by Shanghai Mass Spectrometry Centre, Shanghai Institute of Organic Chemistry, CAS (Chinese Academic of Sciences).

**General procedure for silver-catalyzed decarboxylative iodination of aryl carboxylic acids (Procedure A).** An oven-dried Schlenk tube equipped with a stir bar was charged with aryl carboxylic acid (0.2 mmol), Ag$_2$SO$_4$ (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc)$_2$ (21.8 mg, 0.12 mmol, 0.6 equiv), NaI (45 mg, 0.3 mmol, 1.5 equiv) and 2,9-dimethyl-1,10-phenanthrolinium (12.5 mg, 0.06 mmol, 0.3 equiv). The tube was fitted with a rubber septum, and then it was evacuated and refilled with dioxygen three times. Under dioxygen, DMSO (4 mL) was added via syringe. The rubber septum was replaced with a Teflon screwcap under dioxygen flow, and the Schlenk tube was pressurized to 1 atm. With stirring, the reaction mixtures were heated at 160 °C for the indicated amount of time (unless otherwise specified), and then cooled down to room temperature. The resultant mixture was filtered through a short plug of silica gel and then concentrated in vacuo. The residue was then purified by flash chromatography on silica gel to provide the corresponding product.

**General procedure for silver-catalyzed decarboxylative bromination and chlorination of aryl carboxylic acids (Procedure B).** An oven-dried Schlenk tube equipped with a stir bar was charged with aryl carboxylic acid (0.2 mmol), Ag$_2$SO$_4$ (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc)$_2$ (36.3 mg, 0.2 mmol, 1 equiv), NaX (0.3 mmol, 1.5 equiv) and 2,9-dimethyl-1,10-phenanthrolinium (12.5 mg, 0.06 mmol, 0.3 equiv). The tube was fitted with a rubber septum, and then it was evacuated and refilled with dioxygen three times. Under dioxygen, DMSO (4 mL) was added via syringe. The rubber septum was replaced with a Teflon screwcap under dioxygen flow, and the Schlenk tube was pressurized to 1 atm. With stirring, the reaction mixtures were heated at 160 °C for the indicated amount of time (unless otherwise specified), and then cooled down to room temperature. The resultant mixture was filtered through a short plug of silica gel and then concentrated in vacuo. The residue was then purified by flash chromatography on silica gel to provide the corresponding product.
General procedure for silver-catalyzed decarboxylative halogenation of 2-chloro-5-nitrobenzoic acid (Procedure C). An oven-dried Schlenk tube equipped with a stir bar was charged with aryl carboxylic acid (0.2 mmol), Ag₂SO₄ (3.1 mg, 0.01 mmol, 0.05 equiv), Cu(OAc)₂ (36.3 mg, 0.2 mmol, 1 equiv) and NaX (0.24 mmol, 1.2 equiv). The tube was fitted with a rubber septum, and then it was evacuated and refilled with dioxygen three times. Under dioxygen, DMSO (2 mL) was added via syringe. The rubber septum was replaced with a Teflon screwcap under dioxygen flow, and the Schlenk tube was pressurized to 1 atm. With stirring, the reaction mixtures were heated at 160 °C for the indicated amount of time (unless otherwise specified), and then cooled down to room temperature. The resultant mixture was filtered through a short plug of silica gel and then concentrated in vacuo. The residue was then purified by flash chromatography on silica gel to provide the corresponding product.

General procedure for silver-catalyzed decarboxylative iodination of electron-rich aryl carboxylic acids (Procedure D). An oven-dried Schlenk tube equipped with a stir bar was charged with aryl carboxylic acid (0.2 mmol), Ag₂SO₄ (3.1 mg, 0.01 mmol, 0.05 equiv), Cu(OAc)₂ (36.3 mg, 0.2 mmol, 1 equiv) and NaI (149.9 mg, 1 mmol, 5 equiv). The tube was fitted with a rubber septum, and then it was evacuated and refilled with dioxygen three times. Under dioxygen, DMSO (1 mL) was added via syringe. The rubber septum was replaced with a Teflon screwcap under dioxygen flow, and the Schlenk tube was pressurized to 1 atm. With stirring, the reaction mixtures were heated at 160 °C for the indicated amount of time (unless otherwise specified), and then cooled down to room temperature. The resultant mixture was filtered through a short plug of silica gel and then concentrated in vacuo. The residue was then purified by flash chromatography on silica gel to provide the corresponding product.

1-Iodo-4,5-dimethoxy-2-nitrobenzene (1a). Procedure A was followed using 4,5-dimethoxy-2-nitrobenzoic acid (45.4 mg, 0.2 mmol), Ag₂SO₄ (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc)₂ (21.8 mg, 0.12 mmol, 0.6 equiv), NaI (45 mg, 0.3 mmol, 1.5 equiv) and 2,9-dimethyl-1,10-phenanthroline (12.5 mg, 0.06 mmol, 0.3 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (10% ether in hexane) to afford 37.1 mg (60%) of the product as a yellow solid. Exhibited spectral data in accordance with previous report.¹ ¹H NMR (400 MHz, CDCl₃): δ 7.61 (s, 1 H), 7.39 (s, 1 H), 3.96 (s, 3 H), 3.93 (s, 3 H). ¹³C NMR (100 MHz, CDCl₃): δ 152.7, 149.1, 145.1, 123.1, 109.0, 77.2, 56.7, 56.4. HRMS (MALDI-TOF) m/z: [M]+ Calcd for C₈H₈INO₄ 308.9498; Found: 308.9496.

1-Bromo-4,5-dimethoxy-2-nitrobenzene (1b). Procedure B was followed using 4,5-dimethoxy-2-nitrobenzoic acid (45.4 mg, 0.2 mmol), Ag₂SO₄ (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc)₂ (36.3 mg, 0.2 mmol, 1 equiv), NaBr (30.9 mg, 0.3 mmol, 1.5 equiv) and 2,9-dimethyl-1,10-phenanthroline (12.5 mg, 0.06 mmol, 0.3 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (10%
ether in hexane) to afford 25.9 mg (49%) of the product as a yellow solid. Exhibited spectral data in accordance with previous report.\textsuperscript{1,3} \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): $\delta$ 7.57 (s, 1 H), 7.12 (s, 1 H), 3.96 (s, 3 H), 3.94 (s, 3 H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): $\delta$ 152.8, 148.2, 141.8, 116.5, 109.0, 107.5, 56.7, 56.5. HRMS (MALDI-TOF) m/z: [M]$^+$ Calcd for C\textsubscript{8}H\textsubscript{8}BrNO\textsubscript{4} 260.9637; Found: 260.9636.

1-Chloro-4,5-dimethoxy-2-nitrobenzene (1c). Procedure B was followed using 4,5-dimethoxy-2-nitrobenzoic acid (45.4 mg, 0.2 mmol), Ag\textsubscript{2}SO\textsubscript{4} (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc\textsubscript{2}) (36.3 mg, 0.2 mmol, 1 equiv) and 2,9-dimethyl-1,10-phenanthroline (12.5 mg, 0.06 mmol, 0.3 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (10% ether in hexane) to afford 22.6 mg (52%) of the product as a yellow solid. Exhibited spectral data in accordance with previous report.\textsuperscript{1,3} \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): $\delta$ 7.55 (s, 1 H), 6.93 (s, 1 H), 3.95 (s, 3 H), 3.93 (s, 3 H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): $\delta$ 152.9, 147.6, 139.7, 121.1, 113.4, 108.6, 56.7, 56.5. HRMS (MALDI-TOF) m/z: [M]$^+$ Calcd for C\textsubscript{8}H\textsubscript{8}ClNO\textsubscript{4} 217.0142; Found: 217.0142.

2-Iodo-4-methoxy-1-nitrobenzene (2a). Procedure A was followed using 5-methoxy-2-nitrobenzoic acid (39.4 mg, 0.2 mmol), Ag\textsubscript{2}SO\textsubscript{4} (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc\textsubscript{2}) (21.8 mg, 0.12 mmol, 0.6 equiv), NaI (45 mg, 0.3 mmol, 1.5 equiv) and 2,9-dimethyl-1,10-phenanthroline (12.5 mg, 0.06 mmol, 0.3 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (3% ether in hexane) to afford 35.2 mg (63%) of the product as a yellow solid. Exhibited spectral data in accordance with previous report.\textsuperscript{1,4} \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): $\delta$ 7.99 (d, $J = 9.1$ Hz, 1 H), 7.53 (d, $J = 2.6$ Hz, 1 H), 6.95 (dd, $J = 2.5$, 9.1 Hz, 1 H), 3.88 (s, 3 H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): $\delta$ 162.5, 145.4, 127.4, 127.1, 114.1, 88.1, 56.1. HRMS (MALDI-TOF) m/z: [M]$^+$ Calcd for C\textsubscript{7}H\textsubscript{6}INO\textsubscript{3} 278.9392; Found: 278.9391.

2-Bromo-4-methoxy-1-nitrobenzene (2b). Procedure B was followed using 5-methoxy-2-nitrobenzoic acid (39.4 mg, 0.2 mmol), Ag\textsubscript{2}SO\textsubscript{4} (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc\textsubscript{2}) (36.3 mg, 0.2 mmol, 1 equiv) 2,9-dimethyl-1,10-phenanthroline (12.5 mg, 0.06 mmol, 0.3 equiv) and NaBr (30.9 mg, 0.3 mmol, 1.5 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (3% ether in hexane) to afford 20.4 mg (44%) of the product as a yellow solid. Exhibited spectral data in accordance with previous report.\textsuperscript{1,4} \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): $\delta$ 7.97 (d, $J = 9.1$ Hz, 1 H), 7.21 (d, $J = 2.3$ Hz, 1 H), 6.91 (dd, $J = 2.2$, 9.1 Hz, 1 H), 3.88 (s, 3 H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): $\delta$ 162.8, 142.5, 127.9, 120.2, 116.7, 113.5, 56.2. HRMS (MALDI-TOF) m/z: [M]$^+$ Calcd for C\textsubscript{7}H\textsubscript{6}BrNO\textsubscript{3} 230.9531; Found: 230.9529.

2-Chloro-4-methoxy-1-nitrobenzene (2c). Procedure B was followed using 5-methoxy-2-nitrobenzoic acid (39.4 mg, 0.2 mmol), Ag\textsubscript{2}SO\textsubscript{4} (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc\textsubscript{2}) (36.3 mg, 0.2 mmol, 1 equiv), NaCl (17.5 mg, 0.3 mmol, 1.5 equiv)
and 2,9-dimethyl-1,10-phenanthrolinium (12.5 mg, 0.06 mmol, 0.3 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (3% ether in hexane) to afford 25.1 mg (67%) of the product as a yellow solid. Exhibited spectral data in accordance with previous report.\textsuperscript{1,3} \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) 7.98 (d, \(J = 9.4\) Hz, 1 H), 7.00 (d, \(J = 2.2\) Hz, 1 H), 6.86 (dd, \(J = 2.1, 9.1\) Hz, 1 H), 3.88 (s, 3 H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \(\delta\) 163.0, 140.6, 129.6, 128.0, 116.8, 113.0, 56.2. HRMS (MALDI-TOF) m/z: [M]+ Calcd for C\textsubscript{7}H\textsubscript{6}ClNO\textsubscript{3} 187.0036; Found: 187.0038.

\textbf{1-Iodo-4-methoxy-2-nitrobenzene (3a).} Procedure A was followed using 4-methoxy-2-nitrobenzoic acid (39.4 mg, 0.2 mmol), Ag\textsubscript{2}SO\textsubscript{4} (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc)\textsubscript{2} (21.8 mg, 0.12 mmol, 0.6 equiv), NaI (45 mg, 0.3 mmol, 1.5 equiv) and 2,9-dimethyl-1,10-phenanthrolinium (12.5 mg, 0.06 mmol, 0.3 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (3% ether in hexane) to afford 35.2 mg (63%) of the product as a yellow solid. Exhibited spectral data in accordance with previous report.\textsuperscript{1,5} \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) 7.84 (d, \(J = 8.8\) Hz, 1 H), 7.37 (d, \(J = 2.9\) Hz, 1 H), 6.85 (dd, \(J = 2.9, 8.7\) Hz, 1 H), 3.84 (s, 3 H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \(\delta\) 160.2, 153.5, 142.1, 120.4, 110.0, 74.4, 56.0. HRMS (MALDI-TOF) m/z: [M]+ Calcd for C\textsubscript{7}H\textsubscript{6}INO\textsubscript{3} 278.9392; Found: 278.9394.

\textbf{1-Bromo-4-methoxy-2-nitrobenzene (3b).} Procedure B was followed using 4-methoxy-2-nitrobenzoic acid (39.4 mg, 0.2 mmol), Ag\textsubscript{2}SO\textsubscript{4} (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc)\textsubscript{2} (36.3 mg, 0.2 mmol, 1 equiv), NaBr (30.9 mg, 0.3 mmol, 1.5 equiv) and 2,9-dimethyl-1,10-phenanthrolinium (12.5 mg, 0.06 mmol, 0.3 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (1% ether in hexane) to afford 31.1 mg (67%) of the product as a yellow solid. Exhibited spectral data in accordance with previous report.\textsuperscript{1} \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) 7.58 (d, \(J = 8.9\) Hz, 1 H), 7.35 (d, \(J = 2.8\) Hz, 1 H), 6.98 (dd, \(J = 2.9, 8.9\) Hz, 1 H), 3.85 (s, 3 H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \(\delta\) 159.2, 150.1, 135.4, 119.8, 110.8, 104.4, 56.1. HRMS (MALDI-TOF) m/z: [M]+ Calcd for C\textsubscript{7}H\textsubscript{6}BrNO\textsubscript{3} 230.9531; Found: 230.9533.

\textbf{1-Chloro-4-methoxy-2-nitrobenzene (3c).} Procedure B was followed using 4-methoxy-2-nitrobenzoic acid (39.4 mg, 0.2 mmol), Ag\textsubscript{2}SO\textsubscript{4} (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc)\textsubscript{2} (36.3 mg, 0.2 mmol, 1 equiv), NaCl (17.5 mg, 0.3 mmol, 1.5 equiv) and 2,9-dimethyl-1,10-phenanthrolinium (12.5 mg, 0.06 mmol, 0.3 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (1% ether in hexane) to afford 19.8 mg (53%) of the product as a yellow solid. Exhibited spectral data in accordance with previous report.\textsuperscript{1} \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) 7.42 (d, \(J = 8.9\) Hz, 1 H), 7.39 (d, \(J = 2.8\) Hz, 1 H), 7.06 (dd, \(J = 2.9, 8.9\) Hz, 1 H), 3.86 (s, 3 H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \(\delta\) 158.5, 148.2, 132.4, 119.8, 118.1, 110.4, 56.1. HRMS (MALDI-TOF) m/z: [M]+ Calcd for C\textsubscript{7}H\textsubscript{6}ClNO\textsubscript{3} 187.0036; Found: 187.0038.
1-Iodo-4-methyl-2-nitrobenzene (4a). Procedure A was followed using 4-methyl-2-nitrobenzoic acid (36.2 mg, 0.2 mmol), Ag$_2$SO$_4$ (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc)$_2$ (21.8 mg, 0.12 mmol, 0.6 equiv), NaI (45 mg, 0.3 mmol, 1.5 equiv) and 2,9-dimethyl-1,10-phenanthrolinium (12.5 mg, 0.06 mmol, 0.3 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (1% ether in hexane) to afford 27.9 mg (53%) of the product as a yellow solid. Exhibited spectral data in accordance with previous report.$^{1,5}$ $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.87 (d, $J$ = 8.1 Hz, 1 H), 7.67 (s, 1 H), 7.08 (d, $J$ = 8.0 Hz, 1 H), 2.39 (s, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 152.8, 141.5, 139.9, 134.4, 125.9, 82.0, 20.8. HRMS (MALDI-TOF) m/z: [M]$^+$ Calcd for C$_7$H$_6$INO$_2$ 262.9443; Found: 262.9447.

1-Bromo-4-methyl-2-nitrobenzene (4b). Procedure B was followed using 4-methyl-2-nitrobenzoic acid (36.2 mg, 0.2 mmol), Ag$_2$SO$_4$ (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc)$_2$ (36.3 mg, 0.2 mmol, 1 equiv), 2,9-dimethyl-1,10-phenanthrolinium (12.5 mg, 0.06 mmol, 0.3 equiv) and NaBr (30.9 mg, 0.3 mmol, 1.5 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (1% ether in hexane) to afford 29.8 mg (69%) of the product as a yellow liquid. Exhibited spectral data in accordance with previous report.$^{1}$ $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.64 (s, 1 H), 7.59 (d, $J$ = 8.2 Hz, 1 H), 7.23 (d, $J$ = 8.2 Hz, 1 H), 2.39 (s, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 149.6, 139.0, 134.6, 134.1, 125.9, 110.9, 20.7. HRMS (MALDI-TOF) m/z: [M]$^+$ Calcd for C$_7$H$_6$BrNO$_2$ 214.9582; Found: 214.9580.

1-Chloro-4-methyl-2-nitrobenzene (4c). Procedure B was followed using 4-methyl-2-nitrobenzoic acid (36.2 mg, 0.2 mmol), Ag$_2$SO$_4$ (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc)$_2$ (36.3 mg, 0.2 mmol, 1 equiv), 2,9-dimethyl-1,10-phenanthrolinium (12.5 mg, 0.06 mmol, 0.3 equiv) and NaCl (17.5 mg, 0.3 mmol, 1.5 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (1% ether in hexane) to afford 17.4 mg (51%) of the product as a yellow liquid. Exhibited spectral data in accordance with previous report.$^{1}$ $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.58 (s, 1 H), 7.30 (m, 2 H), 2.34 (s, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 147.5, 138.5, 134.0, 131.3, 125.7, 123.5, 20.5. HRMS (MALDI-TOF) m/z: [M]$^+$ Calcd for C$_7$H$_6$ClNO$_2$ 171.0087; Found: 171.0089.

2-Iodo-1-methyl-3-nitrobenzene (5a). Procedure A was followed using 2-methyl-6-nitrobenzoic acid (36.2 mg, 0.2 mmol), Ag$_2$SO$_4$ (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc)$_2$ (21.8 mg, 0.12 mmol, 0.6 equiv), NaI (45 mg, 0.3 mmol, 1.5 equiv) and 2,9-dimethyl-1,10-phenanthrolinium (12.5 mg, 0.06 mmol, 0.3 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (1% ether in hexane) to afford 14.2 mg (27%) of the product as a yellow solid. Exhibited spectral data in accordance with previous report.$^{1,6}$ $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.42 (d, $J$ = 7.7 Hz, 1 H), 7.36 - 7.31 (m, 1 H), 2.58 (s, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 145.2, 132.3, 128.6, 121.8, 110.0, 92.4, 29.7. HRMS (MALDI-TOF) m/z: [M]$^+$ Calcd for C$_7$H$_6$INO$_2$ 262.9443; Found: 262.9441.
2-Bromo-1-methyl-3-nitrobenzene (5b). Procedure B was followed using 2-methyl-6-nitrobenzoic acid (36.2 mg, 0.2 mmol), Ag$_2$SO$_4$ (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc)$_2$ (36.3 mg, 0.2 mmol, 1 equiv), 2,9-dimethyl-1,10-phenanthrolinium (12.5 mg, 0.06 mmol, 0.3 equiv) and NaBr (30.9 mg, 0.3 mmol, 1.5 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (1% ether in hexane) to afford 13.0 mg (30%) of the product as a yellow liquid. Exhibited spectral data in accordance with previous report.$^{1,7}$ $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.52 (d, $J$ = 7.9 Hz, 1 H), 7.43 (d, $J$ = 7.4 Hz, 1 H), 7.33 (t, $J$ = 7.8 Hz, 1 H), 2.52 (s, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 151.3, 141.3, 133.5, 127.6, 122.3, 115.8, 23.6. HRMS (MALDI-TOF) m/z: [M]$^+$ Calcd for C$_7$H$_6$BrNO$_2$ 214.9582; Found: 214.9584.

2-Chloro-1-methyl-3-nitrobenzene (5c). Procedure B was followed using 2-methyl-6-nitrobenzoic acid (36.2 mg, 0.2 mmol), Ag$_2$SO$_4$ (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc)$_2$ (36.3 mg, 0.2 mmol, 1 equiv), 2,9-dimethyl-1,10-phenanthrolinium (12.5 mg, 0.06 mmol, 0.3 equiv) and NaCl (17.5 mg, 0.3 mmol, 1.5 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (1% ether in hexane) to afford 14.7 mg (43%) of the product as a yellow liquid. Exhibited spectral data in accordance with previous report.$^3$ $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.58 (d, $J$ = 8.0 Hz, 1 H), 7.44 (d, $J$ = 8.0 Hz, 1 H), 7.29 (t, $J$ = 8.0 Hz, 1 H), 2.46 (s, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 149.0, 139.4, 134.0, 126.8, 125.9, 122.5, 20.3. HRMS (MALDI-TOF) m/z: [M]$^+$ Calcd for C$_7$H$_6$ClNO$_2$ 171.0087; Found: 171.0089.

1-Iodo-2-nitrobenzene (6a). Procedure A was followed using 2-nitrobenzoic acid (33.4 mg, 0.2 mmol), Ag$_2$SO$_4$ (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc)$_2$ (21.8 mg, 0.12 mmol, 0.6 equiv), 2,9-dimethyl-1,10-phenanthrolinium (12.5 mg, 0.06 mmol, 0.3 equiv) and NaI (45 mg, 0.3 mmol, 1.5 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (1% ether in hexane) to afford 19.6 mg (39%) of the product as a yellow solid. Exhibited spectral data in accordance with previous report.$^1$ $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.04 (dd, $J$ =1.0, 7.9 Hz, 1 H), 7.85 (dd, $J$ = 1.3, 8.1 Hz, 1 H), 7.51 - 7.47 (m, 1 H), 7.28 - 7.24 (m, 1 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 153.0, 141.9, 133.4, 129.1, 125.4, 86.2. HRMS (MALDI-TOF) m/z: [M]$^+$ Calcd for C$_6$H$_4$INO$_2$ 248.9287; Found: 248.9285.

1-Bromo-2-nitrobenzene (6b). Procedure B was followed using 2-nitrobenzoic acid (33.4 mg, 0.2 mmol), Ag$_2$SO$_4$ (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc)$_2$ (36.3 mg, 0.2 mmol, 1 equiv), 2,9-dimethyl-1,10-phenanthrolinium (12.5 mg, 0.06 mmol, 0.3 equiv) and NaBr (30.9 mg, 0.3 mmol, 1.5 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (1% ether in hexane) to afford 20.2 mg (50%) of the product as a yellow liquid. Exhibited spectral data in accordance with previous report.$^{1,3}$ $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.84 (dd, $J$ =1.8, 7.4 Hz, 1 H), 7.75 (dd, $J$ = 1.5, 7.2 Hz, 1 H), 7.52 - 7.37 (m, 2 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 149.8, 135.0, 133.2, 128.3, 125.6, 114.4. HRMS (MALDI-TOF) m/z: [M]$^+$ Calcd for C$_6$H$_4$BrNO$_2$ 200.9425; Found: 200.9424.
1-Chloro-2-nitrobenzene (6c). Procedure B was followed using 2-nitrobenzoic acid (33.4 mg, 0.2 mmol), \( \text{Ag}_2\text{SO}_4 \) (6.2 mg, 0.02 mmol, 0.1 equiv), \( \text{Cu(OAc)}_2 \) (36.3 mg, 0.2 mmol, 1 equiv), 2,9-dimethyl-1,10-phenanthrolinium (12.5 mg, 0.06 mmol, 0.3 equiv) and \( \text{NaCl} \) (17.5 mg, 0.3 mmol, 1.5 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (1% ether in hexane) to afford 14.1 mg (45%) of the product as a yellow liquid. Exhibited spectral data in accordance with previous report. \(^{1,3}\) \( ^1\text{H} \text{NMR (400 MHz, CDCl}_3\text{): } \delta \) 7.86 (d, \( J = 8.0 \text{ Hz, 1 H} \)), 7.56 - 7.50 (m, 2 H), 7.44 - 7.39 (m, 1 H). \( ^{13}\text{C} \text{NMR (100 MHz, CDCl}_3\text{): } \delta \) 147.9, 133.3, 131.8, 127.7, 126.8, 125.5. HRMS (MALDI-TOF) \( m/z: [M]^+ \) Calcd for \( \text{C}_6\text{H}_4\text{ClNO}_2 \) 156.9931; Found: 156.9931.

1-Iodo-2-nitro-4-(trifluoromethyl)benzene (7a). Procedure A was followed using 1-iodo-2-nitro-4-(trifluoromethyl)benzoic acid (47.0 mg, 0.2 mmol), \( \text{Ag}_2\text{SO}_4 \) (6.2 mg, 0.02 mmol, 0.1 equiv), \( \text{Cu(OAc)}_2 \) (21.8 mg, 0.12 mmol, 0.6 equiv), \( \text{NaI} \) (45 mg, 0.3 mmol, 1.5 equiv) and 2,9-dimethyl-1,10-phenanthrolinium (12.5 mg, 0.06 mmol, 0.3 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (1% ether in hexane) to afford 29.8 mg (47%) of the product as a yellow solid. Exhibited spectral data in accordance with previous report. \(^{1,5}\) \( ^1\text{H} \text{NMR (400 MHz, CDCl}_3\text{): } \delta \) 8.22 (d, \( J = 8.3 \text{ Hz, 1 H} \)), 8.11 (d, \( J = 1.2 \text{ Hz, 1 H} \)), 7.52 (dd, \( J = 1.5, 8.3 \text{ Hz, 1 H} \)). \( ^{13}\text{C} \text{NMR (100 MHz, CDCl}_3\text{): } \delta \) 153.1, 143.1, 131.9 (q, \( J = 34.9 \text{ Hz} \)), 129.6 (q, \( J = 3.0 \text{ Hz} \)), 122.6 (q, \( J = 271.6 \text{ Hz} \)), 122.3 (q, \( J = 3.8 \text{ Hz} \)), 90.9. \(^{19}\text{F} \text{NMR (377 MHz, CDCl}_3\text{): } \delta \) - 63.3 (s, 3 F). HRMS (MALDI-TOF) \( m/z: [M]^+ \) Calcd for \( \text{C}_7\text{H}_3\text{F}_3\text{INO}_2 \) 316.9161; Found: 316.9159.

1-Bromo-2-nitro-4-(trifluoromethyl)benzene (7b). Procedure B was followed using 2-nitro-4-(trifluoromethyl)benzoic acid (47.0 mg, 0.2 mmol), \( \text{Ag}_2\text{SO}_4 \) (6.2 mg, 0.02 mmol, 0.1 equiv), \( \text{Cu(OAc)}_2 \) (36.3 mg, 0.2 mmol, 1 equiv), \( \text{NaBr} \) (30.9 mg, 0.3 mmol, 1.5 equiv) and 2,9-dimethyl-1,10-phenanthrolinium (12.5 mg, 0.06 mmol, 0.3 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (1% ether in hexane) to afford 16.2 mg (30%) of the product as a yellow liquid. Exhibited spectral data in accordance with previous report. \(^1\) \( ^1\text{H} \text{NMR (400 MHz, CDCl}_3\text{): } \delta \) 8.11 (s, 1 H), 7.91 (d, \( J = 8.4 \text{ Hz, 1 H} \)), 7.69 (d, \( J = 8.3 \text{ Hz, 1 H} \)). \( ^{13}\text{C} \text{NMR (100 MHz, CDCl}_3\text{): } \delta \) 149.9, 136.1, 131.1 (q, \( J = 34.1 \text{ Hz} \)), 129.5 (q, \( J = 3.8 \text{ Hz} \)), 122.8 (q, \( J = 3.8 \text{ Hz} \)), 122.5 (q, \( J = 271.6 \text{ Hz} \)), 118.4. \(^{19}\text{F} \text{NMR (377 MHz, CDCl}_3\text{): } \delta \) - 63.1 (s, 1 F). HRMS (MALDI-TOF) \( m/z: [M]^+ \) Calcd for \( \text{C}_7\text{H}_3\text{BrF}_3\text{NO}_2 \) 268.9299; Found: 268.9301.

1-Chloro-2-nitro-4-(trifluoromethyl)benzene (7c). Procedure B was followed using 2-nitro-4-(trifluoromethyl)benzoic acid (47.0 mg, 0.2 mmol), \( \text{Ag}_2\text{SO}_4 \) (6.2 mg, 0.02 mmol, 0.1 equiv), \( \text{Cu(OAc)}_2 \) (36.3 mg, 0.2 mmol, 1 equiv), \( \text{NaCl} \) (17.5 mg, 0.3 mmol, 1.5 equiv) and 2,9-dimethyl-1,10-phenanthrolinium (12.5 mg, 0.06 mmol, 0.3 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (1% ether in hexane) to afford 7.2 mg (16%) of the product as a yellow liquid. Exhibited spectral data in accordance with previous report. \(^1\) \( ^1\text{H} \text{NMR (400 MHz, CDCl}_3\text{): } \delta \) 8.11 (s, 1 H), 7.91 (d, \( J = 8.4 \text{ Hz, 1 H} \)), 7.69 (d, \( J = 8.3 \text{ Hz, 1 H} \)). \( ^{13}\text{C} \text{NMR (100 MHz, CDCl}_3\text{): } \delta \) 149.9, 136.1, 131.1 (q, \( J = 34.1 \text{ Hz} \)), 129.5 (q, \( J = 3.8 \text{ Hz} \)), 122.8 (q, \( J = 3.8 \text{ Hz} \)), 122.5 (q, \( J = 271.6 \text{ Hz} \)), 118.4. \(^{19}\text{F} \text{NMR (377 MHz, CDCl}_3\text{): } \delta \) - 63.1 (s, 1 F). HRMS (MALDI-TOF) \( m/z: [M]^+ \) Calcd for \( \text{C}_7\text{H}_3\text{BrF}_3\text{NO}_2 \) 268.9299; Found: 268.9301.
CDCl$_3$: $\delta$ 8.11 (s, 1H), 7.80 - 7.72 (m, 2 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 147.8, 132.9, 130.9, 130.3 (q, $J = 34.9$ Hz), 129.6 (q, $J = 3.8$ Hz), 122.8 (q, $J = 3.8$ Hz), 122.4 (q, $J = 270.9$ Hz). $^{19}$F NMR (377 MHz, CDCl$_3$): $\delta$ - 63.0 (s, 3 F). HRMS (MALDI-TOF) m/z: [M]$^+$ Calcd for C$_7$H$_3$ClF$_3$NO$_2$ 224.9804; Found: 224.9807.

4-Fluoro-1-iodo-2-nitrobenzene (8a). Procedure A was followed using 4-fluoro-2-nitrobenzoic acid (37.0 mg, 0.2 mmol), Ag$_2$SO$_4$ (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc)$_2$ (21.8 mg, 0.12 mmol, 0.6 equiv), NaI (45 mg, 0.3 mmol, 1.5 equiv) and 2,9-dimethyl-1,10-phenanthrolinium (12.5 mg, 0.06 mmol, 0.3 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (1% ether in hexane) to afford 35.2 mg (66%) of the product as a yellow liquid. Exhibited spectral data in accordance with previous report.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.02 (q, $J = 4.0$ Hz, 1 H), 7.64 (dd, $J = 2.8$, 8.0 Hz, 1 H), 7.07 (ddd, $J = 2.8$, 7.5, 8.6 Hz, 1 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 162.2 (d, $J = 251.9$ Hz), 153.4, 143.1 (d, $J = 7.6$ Hz), 121.2 (d, $J = 21.2$ Hz), 113.6 (d, $J = 26.5$ Hz), 79.6 (d, $J = 3.8$ Hz). $^{19}$F NMR (377 MHz, CDCl$_3$): $\delta$ - 109.6 - - 109.7 (m, 1 F). HRMS (MALDI-TOF) m/z: [M]$^+$ Calcd for C$_6$H$_3$FINO$_2$ 266.9192; Found: 266.9196.

1-Bromo-4-fluoro-2-nitrobenzene (8b). Procedure B was followed using 4-fluoro-2-nitrobenzoic acid (37.0 mg, 0.2 mmol), Ag$_2$SO$_4$ (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc)$_2$ (36.3 mg, 0.2 mmol, 1 equiv), 2,9-dimethyl-1,10-phenanthrolinium (30.9 mg, 0.3 mmol, 1.5 equiv) and NaBr (30.9 mg, 0.3 mmol, 1.5 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (1% ether in hexane) to afford 21.2 mg (48%) of the product as a yellow liquid. Exhibited spectral data in accordance with previous report.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.73 (q, $J = 4.0$ Hz, 1 H), 7.60 (dd, $J = 2.6$, 7.7 Hz, 1 H), 7.21 (td, $J = 4.0$, 8.0 Hz, 1 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 161.1 (d, $J = 251.1$ Hz), 150.0, 136.4 (d, $J = 7.6$ Hz), 120.9 (d, $J = 21.2$ Hz), 113.5 (d, $J = 27.3$ Hz), 109.1 (d, $J = 4.6$ Hz). $^{19}$F NMR (377 MHz, CDCl$_3$): $\delta$ - 110.2 (dd, $J = 7.4$, 12.7 Hz, 1 F). HRMS (MALDI-TOF) m/z: [M]$^+$ Calcd for C$_6$H$_3$BrFNO$_2$ 218.9331; Found: 218.9333.

1-Chloro-4-fluoro-2-nitrobenzene (8c). Procedure B was followed using 4-fluoro-2-nitrobenzoic acid (37.0 mg, 0.2 mmol), Ag$_2$SO$_4$ (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc)$_2$ (36.3 mg, 0.2 mmol, 1 equiv), NaCl (17.5 mg, 0.3 mmol, 1.5 equiv) and 2,9-dimethyl-1,10-phenanthrolinium (12.5 mg, 0.06 mmol, 0.3 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (1% ether in hexane) to afford 14.7 mg (42%) of the product as a yellow liquid. Exhibited spectral data in accordance with previous report.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.62 (dd, $J = 2.2$, 7.5 Hz, 1 H), 7.54 (q, $J = 4.0$ Hz, 1 H), 7.27 (dd, $J = 2.3$, 7.6 Hz, 1 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 160.4 (d, $J = 251.2$ Hz), 148.1, 133.2 (d, $J = 7.6$ Hz), 122.5 (d, $J = 3.8$ Hz), 120.8 (d, $J = 22.0$ Hz), 113.3 (d, $J = 27.3$ Hz). $^{19}$F NMR (377 MHz, CDCl$_3$): $\delta$ - 110.7 - - 110.6 (m, 1 F). HRMS (MALDI-TOF) m/z: [M]$^+$ Calcd for C$_6$H$_3$ClFNO$_2$ 174.9836; Found: 174.9830.
4-Chloro-2-iodo-1-nitrobenzene (9a). Procedure A was followed using 5-chloro-2-nitrobenzoic acid (40.3 mg, 0.2 mmol), Ag₂SO₄ (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc)₂ (21.8 mg, 0.12 mmol, 0.6 equiv), NaI (45 mg, 0.3 mmol, 1.5 equiv) and 2,9-dimethyl-1,10-phenanthrolinium (12.5 mg, 0.06 mmol, 0.3 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (1% ether in hexane) to afford 43 mg (76%) of the product as a yellow solid. Exhibited spectral data in accordance with previous report.¹ ¹H NMR (400 MHz, CDCl₃): δ 8.04 (d, J = 2.1 Hz, 1 H), 7.84 (d, J = 8.7 Hz, 1 H), 7.46 (dd, J = 2.1, 8.7 Hz, 1 H). ¹³C NMR (100 MHz, CDCl₃): δ 151.2, 141.4, 139.3, 129.2, 126.3, 87.1. HRMS (MALDI-TOF) m/z: [M]+ Calcd for C₆H₃ClINO₂ 282.8897; Found: 282.8895.

2-Bromo-4-chloro-1-nitrobenzene (9b). Procedure B was followed using 5-chloro-2-nitrobenzoic acid (40.3 mg, 0.2 mmol), Ag₂SO₄ (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc)₂ (36.3 mg, 0.2 mmol, 1 equiv), NaBr (30.9 mg, 0.3 mmol, 1.5 equiv) and 2,9-dimethyl-1,10-phenanthrolinium (12.5 mg, 0.06 mmol, 0.3 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (1% ether in hexane) to afford 32.6 mg (69%) of the product as a yellow liquid. Exhibited spectral data in accordance with previous report.³ ¹H NMR (400 MHz, CDCl₃): δ 7.84 (d, J = 8.0 Hz, 1 H), 7.76 (s, 1 H), 7.44 (d, J = 8.0 Hz, 1 H). ¹³C NMR (100 MHz, CDCl₃): δ 148.1, 139.2, 134.8, 128.5, 126.7, 115.6. HRMS (MALDI-TOF) m/z: [M]+ Calcd for C₆H₃BrClNO₂ 234.9036; Found: 234.9038.

2,4-Dichloro-1-nitrobenzene (9c). Procedure B was followed using 5-chloro-2-nitrobenzoic acid (40.3 mg, 0.2 mmol), Ag₂SO₄ (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc)₂ (36.3 mg, 0.2 mmol, 1 equiv), 2,9-dimethyl-1,10-phenanthrolinium (12.5 mg, 0.06 mmol, 0.3 equiv) and NaCl (17.5 mg, 0.3 mmol, 1.5 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (1% ether in hexane) to afford 24.7 mg (64%) of the product as a yellow liquid. Exhibited spectral data in accordance with previous report.³ ¹H NMR (400 MHz, CDCl₃): δ 7.86 (d, J = 8.7 Hz, 1 H), 7.55 (d, J = 1.8 Hz, 1 H), 7.40 (dd, J = 1.7, 8.7 Hz, 1 H). ¹³C NMR (100 MHz, CDCl₃): δ 146.2, 139.3, 131.8, 128.5, 127.9, 126.7. HRMS (MALDI-TOF) m/z: [M]+ Calcd for C₆H₃Cl₂NO₂ 190.9541; Found: 190.9542.

4-Chloro-1-iodo-2-nitrobenzene (10a). Procedure A was followed using 4-chloro-2-nitrobenzoic acid (40.3 mg, 0.2 mmol), Ag₂SO₄ (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc)₂ (21.8 mg, 0.12 mmol, 0.6 equiv), NaI (45 mg, 0.3 mmol, 1.5 equiv) and 2,9-dimethyl-1,10-phenanthrolinium (12.5 mg, 0.06 mmol, 0.3 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (1% ether in hexane) to afford 40.8 mg (72%) of the product as a yellow solid. Exhibited spectral data in accordance with previous report.¹⁵ ¹H NMR (400 MHz, CDCl₃): δ 7.95 (d, J = 8.5 Hz, 1 H), 7.84 (d, J = 2.0 Hz, 1 H), 7.28 - 7.25 (m, 1 H). ¹³C NMR (100 MHz, CDCl₃): δ 153.2, 142.7, 135.3, 133.7, 125.6, 83.8. HRMS (MALDI-TOF) m/z: [M]+ Calcd for C₆H₃IINO₂ 282.8897; Found: 282.8902.
1-Bromo-4-chloro-2-nitrobenzene (10b). Procedure B was followed using 4-chloro-2-nitrobenzoic acid (40.3 mg, 0.2 mmol), Ag$_2$SO$_4$ (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc)$_2$ (36.3 mg, 0.2 mmol, 1 equiv), 2,9-dimethyl-1,10-phenanthrolinium (12.5 mg, 0.06 mmol, 0.3 equiv) and NaBr (30.9 mg, 0.3 mmol, 1.5 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (1% ether in hexane) to afford 30.2 mg (64%) of the product as a yellow liquid. Exhibited spectral data in accordance with previous report.$^1$ $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.83 (d, $J = 2.1$ Hz, 1 H), 7.67 (d, $J = 8.6$ Hz, 1 H), 7.42 (dd, $J = 2.2$, 8.5 Hz, 1 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 150.0, 135.9, 134.3, 133.3, 125.7, 112.5. HRMS (MALDI-TOF) m/z: [M]$^+$ Calcd for C$_6$H$_3$BrClNO$_2$ 234.9036; Found: 234.9033.

1,4-Dichloro-2-nitrobenzene (10c). Procedure B was followed using 4-chloro-2-nitrobenzoic acid (40.3 mg, 0.2 mmol), Ag$_2$SO$_4$ (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc)$_2$ (36.3 mg, 0.2 mmol, 1 equiv), 2,9-dimethyl-1,10-phenanthrolinium (12.5 mg, 0.06 mmol, 0.3 equiv) and NaCl (17.5 mg, 0.3 mmol, 1.5 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (1% ether in hexane) to afford 20.7 mg (54%) of the product as a yellow liquid. Exhibited spectral data in accordance with previous report.$^1$ $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.87 (s, 1 H), 7.50 (d, $J = 0.8$ Hz, 2 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 148.1, 133.5, 133.3, 132.8, 125.6, 125.5. HRMS (MALDI-TOF) m/z: [M]$^+$ Calcd for C$_6$H$_3$Cl$_2$NO$_2$ 190.9541; Found: 190.9543.

1-Chloro-2-iodo-4-nitrobenzene (11a). Procedure C was followed using 2-Chloro-5-nitrobenzoic acid (40.3 mg, 0.2 mmol), Ag$_2$SO$_4$ (3.1 mg, 0.01 mmol, 0.05 equiv), Cu(OAc)$_2$ (36.3 mg, 0.2 mmol, 1 equiv) and NaI (36 mg, 0.24 mmol, 1.2 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (1% ether in hexane) to afford a mixture of the desired decarboxylative iodination product 15.8 mg (28%) and by-product 2,4-dichloro-1-nitrobenzene 9c 14.8 mg (39%) as a white solid. Exhibited spectral data in accordance with previous report.$^{1,12}$ 1-Chloro-2-iodo-4-nitrobenzene $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.70 (s, 1 H), 8.16 (d, $J = 8$ Hz, 1 H), 7.61 (d, $J = 8$ Hz, 1 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 135.1, 129.6, 124.1. HRMS (MALDI-TOF) m/z: [M]$^+$ Calcd for C$_6$H$_3$IINO$_2$ 282.8897; Found: 282.8895. By-product 2,4-dichloro-1-nitrobenzene $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.88 (d, $J = 8.7$ Hz, 1 H), 7.58 (d, $J = 1.8$ Hz, 1 H), 7.40 (dd, $J = 1.7$, 8.7 Hz, 1 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 131.8, 127.9, 126.7. HRMS (MALDI-TOF) m/z: [M]$^+$ Calcd for C$_6$H$_3$IINO$_2$ 282.8897; Found: 282.8895.

2-Bromo-1-chloro-4-nitrobenzene (11b). Procedure C was followed using 2-chloro-5-nitrobenzoic acid (40.3 mg, 0.2 mmol), Ag$_2$SO$_4$ (3.1 mg, 0.01 mmol, 0.05 equiv), Cu(OAc)$_2$ (36.3 mg, 0.2 mmol, 1 equiv) and NaBr (24.7 mg, 0.24 mmol, 1.2 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (1% ether in hexane) to afford 17.0 mg (36%) of the product as a white solid. Exhibited spectral data in accordance with previous report.$^{13}$ $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.51 (s, 1 H), 8.13 (d, $J = 8.0$ Hz, 1 H), 7.64 (d, $J = 8.0$ Hz, 1 H). $^{13}$C NMR
(100 MHz, CDCl$_3$): $\delta$ 146.6, 141.8, 130.8, 128.8, 123.3, 123.2. HRMS (MALDI-TOF) m/z: [M]$^+$ Calcd for C$_6$H$_3$BrClNO$_2$ 234.9036; Found: 234.9039.

1,2-Dichloro-4-nitrobenzene (11c). Procedure C was followed using 2-chloro-5-nitrobenzoic acid (40.3 mg, 0.2 mmol), Ag$_2$SO$_4$ (3.1 mg, 0.01 mmol, 0.05 equiv), Cu(OAc)$_2$ (36.3 mg, 0.2 mmol, 1 equiv) and NaCl (14.0 mg, 0.24 mmol, 1.2 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (1% ether in hexane) to afford 15.0 mg (39%) of the product as a white solid. Exhibited spectral data in accordance with previous report.$^{14}$ $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.51 (s, 1 H), 8.09 (d, $J$ = 12.0 Hz, 1 H), 7.65 (d, $J$ = 12.0 Hz, 1 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 146.7, 139.8, 133.9, 131.0, 125.5, 122.5. HRMS (MALDI-TOF) m/z: [M]$^+$ Calcd for C$_6$H$_3$Cl$_2$NO$_2$ 190.9541; Found: 190.9546.

1-Iodo-2,4,5-trimethoxybenzene (12a). Procedure D was followed using 2,4,5-trimethoxybenzoic acid (42.4 mg, 0.2 mmol), Ag$_2$SO$_4$ (3.1 mg, 0.01 mmol, 0.05 equiv), Cu(OAc)$_2$ (36.3 mg, 0.2 mmol, 1 equiv) and NaI (149.9 mg, 1 mmol, 5 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (10% ether in hexane) to afford 21.8 mg (37%) of the product as a white solid. Exhibited spectral data in accordance with previous report.$^{15}$ $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.20 (s, 1 H), 6.51 (s, 1 H), 3.89 (s, 3 H), 3.85 (s, 3 H), 3.83 (s, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 153.0, 150.2, 144.2, 121.8, 97.7, 72.9, 57.3, 56.7, 56.1. HRMS (MALDI-TOF) m/z: [M]$^+$ Calcd for C$_9$H$_{11}$IO$_3$ 293.9753; Found: 293.9751.

2-Iodo-1,3,5-trimethoxybenzene (13a). Procedure D was followed using 2,4,6-trimethoxybenzoic acid (42.4 mg, 0.2 mmol), Ag$_2$SO$_4$ (3.1 mg, 0.01 mmol, 0.05 equiv), Cu(OAc)$_2$ (36.3 mg, 0.2 mmol, 1 equiv) and NaI (149.9 mg, 1 mmol, 5 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (10% ether in hexane) to afford 46.5 mg (79%) of the product as a white solid. Exhibited spectral data in accordance with previous report.$^{16}$ $^1$H NMR(400 MHz, CDCl$_3$): $\delta$ 6.14 (s, 2 H), 3.86 (s, 6 H), 3.83 (s, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 162.1, 159.8, 91.2, 66.7, 56.5, 55.5. HRMS (MALDI-TOF) m/z: [M]$^+$ Calcd for C$_9$H$_{11}$IO$_3$ 293.9753; Found: 293.9755.

3-Chloro-2-iodobenz[b]thiophene (14a). Procedure A was followed using 3-chlorobenz[b]thiophene-2-carboxylic acid (42.5 mg, 0.2 mmol), Ag$_2$SO$_4$ (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc)$_2$ (21.8 mg, 0.12 mmol, 0.6 equiv), NaI (45 mg, 0.3 mmol, 1.5 equiv) and 2,9-dimethyl-1,10-phenanthrolinium (12.5 mg, 0.06 mmol, 0.3 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (1% ether in hexane) to afford 41.2 mg (70%) of the product as a yellow solid. Exhibited spectral data in accordance with previous report.$^1$ $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.76 (dd, $J$ = 8.0, 20.0 Hz, 2 H), 7.44 - 7.32 (m, 2 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 142.1, 135.8, 128.6, 125.4, 125.2, 122.0, 121.9, 78.7. HRMS (MALDI-TOF) m/z: [M]$^+$ Calcd for C$_9$H$_7$I$_2$S 293.8767; Found: 293.8771.
2-Bromo-3-chlorobenzo[b]thiophene (14b). Procedure B was followed using 3-chlorobenzo[b]thiophene-2-carboxylic acid (42.5 mg, 0.2 mmol), Ag$_2$SO$_4$ (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc)$_2$ (36.3 mg, 0.2 mmol, 1 equiv), NaBr (30.9 mg, 0.3 mmol, 1.5 equiv) and 2,9-dimethyl-1,10-phenanthroline (12.5 mg, 0.06 mmol, 0.3 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (1% ether in hexane) to afford 37.5 mg (76%) of the product as a white solid. Exhibited spectral data in accordance with previous report.\textsuperscript{1} \textsuperscript{1}H NMR (400 MHz, CDCl$_3$): $\delta$ 7.78 - 7.69 (m, 2 H), 7.50 - 7.33 (m, 2 H). \textsuperscript{13}C NMR (100 MHz, CDCl$_3$): $\delta$ 138.0, 135.8, 125.7, 125.4, 123.3, 122.0, 121.8, 111.7. HRMS (MALDI-TOF) m/z: [M]$^+$ Calcd for C$_8$H$_4$BrClS 245.8906; Found: 245.8907.

2,3-Dichlorobenzo[b]thiophene (14c). Procedure B was followed using 3-chlorobenzo[b]thiophene-2-carboxylic acid (42.5 mg, 0.2 mmol), Ag$_2$SO$_4$ (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc)$_2$ (36.3 mg, 0.2 mmol, 1 equiv), NaCl (17.5 mg, 0.3 mmol, 1.5 equiv) and 2,9-dimethyl-1,10-phenanthroline (12.5 mg, 0.06 mmol, 0.3 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (1% ether in hexane) to afford 27.6 mg (68%) of the product as a white solid. Exhibited spectral data in accordance with previous report.\textsuperscript{1} \textsuperscript{1}H NMR (400 MHz, CDCl$_3$): $\delta$ 7.94 (d, $J$ = 8.0 Hz, 1 H), 7.85 (d, $J$ = 8.0 Hz, 1 H), 7.64 - 7.55 (m, 2 H). \textsuperscript{13}C NMR (100 MHz, CDCl$_3$): $\delta$ 139.1, 134.5, 129.0, 126.4, 123.6, 122.9, 112.4, 105.5. HRMS (MALDI-TOF) m/z: [M]$^+$ Calcd for C$_8$H$_4$Cl$_2$S 201.9411; Found: 201.9414.

The quantitative data of mass balance for the model reaction

The model reaction was performed in an oven-dried Schlenk tube with a stir bar at 160 °C for 20 hours, which was charged with 4,5-dimethoxy-2-nitrobenzoic acid I (45.4 mg, 0.2 mmol), Ag$_2$SO$_4$ (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc)$_2$ (21.8 mg, 0.12 mmol, 0.6 equiv), NaI (45 mg, 0.3 mmol, 1.5 equiv), 2,9-dimethyl-1,10-phenanthroline (12.5 mg, 0.06 mmol, 0.3 equiv) and DMSO (4 mL) under aerobic conditions. After 20 hours of heating at the indicated temperature, the residue was purified by flash chromatography on silica gel to provide the desired iododecarboxylation product 1-iodo-4,5-dimethoxy-2-nitrobenzene 1a 37.1 mg (60% yield) and by-products that contained protodecarboxylation 5.1 mg (14% yield), decarboxylative cyanation 2.5 mg (6% yield) and other unidentified compounds 1.7 mg. Therefore, it's more than 95% conversion was observed for the transformation of substrate 4,5-dimethoxy-2-nitrobenzoic acid I.

Besides the corresponding decarboxylative product, by-products containing protodecarboxylation, decarboxylative cyanation, methyl benzoate and other unidentified compounds were also detected for other aryl carboxylic acid substrate in this Ag/Cu-mediated decarboxylative halogenation protocol.
Gram-scale synthesis of 4-chloro-1-iodo-2-nitrobenzene 10a

Procedure A was followed using 4-chloro-2-nitrobenzoic acid (1.21 g, 6 mmol), Ag₂SO₄ (187.2 mg, 0.6 mmol, 0.1 equiv), Cu(OAc)₂ (654 mg, 3.6 mmol, 0.6 equiv), NaI (1.35 g, 9 mmol, 1.5 equiv) and 2,9-dimethyl-1,10-phenanthrolinium (375 mg, 1.8 mmol, 0.3 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (1% ether in hexane) to afford product 10a (1.20 g, 71%) as a yellow solid.

Three-step synthesis of iniparib 16

1) Decarboxylative iodination of 4-methyl-2-nitrobenzoic acid 4 with NaI under standard conditions

Procedure A was followed using 4-methyl-2-nitrobenzoic acid (36.2 mg, 0.2 mmol), Ag₂SO₄ (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc)₂ (21.8 mg, 0.12 mmol, 0.6 equiv), NaI (45 mg, 0.3 mmol, 1.5 equiv) and 2,9-dimethyl-1,10-phenanthrolinium (12.5 mg, 0.06 mmol, 0.3 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (1% ether in hexane) to afford 27.9 mg (53%) of the product as a yellow solid.

2) Oxidation of 4-methyl-2-nitrobenzoic acid 4a to 4-iodo-3-nitrobenzoic acid 15 by CrO₃/ H₅IO₆ under mild conditions

An oven-dried Schlenk tube equipped with a stir bar was charged with 4-methyl-2-nitrobenzoic acid (168.6 mg, 0.6 mmol), CrO₃ (30 mg, 0.3 mmol, 0.5 equiv), H₅IO₆ (34.2 mg, 0.3 mmol, 0.5 equiv). The tube was fitted with a rubber septum, and then it was evacuated and refilled with dioxygen three times. Under dioxygen, CH₃CN (5 mL) was added via syringe. The rubber septum was replaced with a Teflon screwcap under dioxygen flow, and the Schlenk tube was pressurized to 1 atm. With stirring, the reaction mixtures were heated at 60 °C for overnight, and then cooled down to room temperature. The reaction mixtures were purified by flash column chromatography on silica gel (2% methanol in dichloromethane) to afford 40.3 mg (23%) of the product (15) as a yellow solid. Exhibited spectral data in accordance with previous report.¹⁸ ¹H NMR (400 MHz, DMSO-d₆): δ 8.32 (s, 1 H), 8.26 (d, J = 8.1 Hz, 1 H), 7.86 (d, J = 8.1 Hz, 1 H); ¹³C NMR (100 MHz, DMSO-d₆): δ 165.6, 153.7, 142.4, 133.8, 132.6, 125.6, 94.4. HRMS (MALDI-TOF) m/z: [M]+ Caled for C₇H₄INO₄ 292.9185; Found: 292.9183.

3) Conversion of 4-iodo-3-nitrobenzoic acid 15 to iniparib 16¹⁹

An oven-dried Schlenk tube equipped with a stir bar was charged with 4-iodo-3-nitrobenzoic acid 15 (58.6 mg, 0.2 mmol), thionyl chloride (0.05 mL, 0.7 mmol, 3.5 equiv). The tube was fitted with a rubber septum, and then it was evacuated and refilled with nitrogen three times. Under nitrogen, toluene (2.0 mL)/ THF (1.0 mL) were added via syringes. The mixture was heated to 80 °C for 2 h. After 2 h, the reaction was allowed to cool, solvents and thionyl chloride were removed under vacuum.
Subsequently, solution of ammonium hydroxide (30% as \( \text{NH}_3 \), 0.6 mL, 9.0 equiv) and THF (2.0 mL) were added into the tube with *in situ* generated acyl chloride via syringes, and the reaction was allowed to stir for 1 h under nitrogen. The phases were separated and the aqueous layer was extracted with ethyl acetate. The organic phases were combined and purified by flash column chromatography on silica gel (ether) to afford 36.2 mg (62%) of the product (\( \text{16} \)) as a yellow solid. Exhibited spectral data in accordance with previous report.\(^{19}\) \(^{1}H\) NMR (400 MHz, DMSO-\(d_6\)): \( \delta \) 7.71 (s, 1 H), 7.85 (dd, \( J = 2.0, 8.5, 1 \) H), 8.22 (d, \( J = 8.5, 1 \) H), 8.24 (s, 1 H), 8.35 (d, \( J = 2.0, 1 \) H); \(^{13}C\) NMR (100 MHz, DMSO-\(d_6\)): \( \delta \) 165.7, 153.7, 142.0, 135.8, 132.5, 124.1, 92.3. HRMS (MALDI-TOF) m/z: [M]\(^+\) Calcd for C\(_7\)H\(_5\)IN\(_2\)O\(_3\) 291.9345; Found: 291.9345.

**Experiments to understand reaction mechanism**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Change of standard conditions</th>
<th>Isolated yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>none [entry 15, Table 1]</td>
<td>60</td>
</tr>
<tr>
<td>2</td>
<td>0.75 equiv I(_2) [instead of NaI]</td>
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</tr>
<tr>
<td>3</td>
<td>0.75 equiv I(_2) [instead of NaI, no Ag/Cu]</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>1 equiv K(_2)PO(_4), 2 equiv I(_2), 1 mL CH(_3)CN, 100 °C [instead of standard condition]</td>
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</tr>
<tr>
<td>5</td>
<td>no Ag</td>
<td>39</td>
</tr>
<tr>
<td>6</td>
<td>no Cu</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>2 equiv TEMPO was added as radical scavenger</td>
<td>9</td>
</tr>
<tr>
<td>8</td>
<td>2 equiv BHT was added as radical scavenger</td>
<td>5</td>
</tr>
</tbody>
</table>

1) **Decarboxylative iodination of 4,5-dimethoxy-2-nitrobenzoic acid 1 with I\(_2\) in the presence of Ag/Cu (entry 2, Table 2)**

An oven-dried Schlenk tube equipped with a stir bar was charged with 4,5-dimethoxy-2-nitrobenzoic acid 1 (45.4 mg, 0.2 mmol), Ag\(_2\)SO\(_4\) (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc)\(_2\) (21.8 mg, 0.12 mmol, 0.6 equiv), I\(_2\) (38.1 mg, 0.15 mmol, 0.75 equiv) and 2,9-dimethyl-1,10-phenanthroline (12.5 mg, 0.06 mmol, 0.3 equiv). The tube was fitted with a rubber septum, and then it was evacuated and refilled with dioxygen three times. Under dioxygen, DMSO (4 mL) was added via syringe. The rubber septum was replaced with a Teflon screwcap under dioxygen flow, and the Schlenk tube was pressurized to 1 atm. With stirring, the reaction mixtures were heated at 160 °C for the indicated amount of time, and then cooled down to room temperature. However, no product was detected via thin layer chromatography (TLC).
2) Decarboxylative iodination of 4,5-dimethoxy-2-nitrobenzoic acid 1 with I₂ in the absence of Ag/Cu (entry 3, Table 2)

An oven-dried Schlenk tube equipped with a stir bar was charged with 4,5-dimethoxy-2-nitrobenzoic acid 1 (45.4 mg, 0.2 mmol), I₂ (38.1 mg, 1.5 mmol, 0.75 equiv) and 2,9-dimethyl-1,10-phenanthroline (12.5 mg, 0.06 mmol, 0.3 equiv). The tube was fitted with a rubber septum, and then it was evacuated and refilled with dioxygen three times. Under dioxygen, DMSO (4 mL) was added via syringe. The rubber septum was replaced with a Teflon screwcap under dioxygen flow, and the Schlenk tube was pressurized to 1 atm. With stirring, the reaction mixtures were heated at 160 °C for the indicated amount of time, and then cooled down to room temperature. However, no product was detected via thin layer chromatography (TLC).

3) Decarboxylative iodination of 4,5-dimethoxy-2-nitrobenzoic acid 1 under Larrosa’s metal-free iododecarboxylation condition²⁰ (entry 4, Table 2)

A oven-dried Schlenk tube equipped with a stir bar was charged with I₂ (101.5 mg, 0.4 mmol, 2 equiv), capped and flushed with N₂. The tube was transferred to a glove box, then 4,5-dimethoxy-2-nitrobenzoic acid 1 (45.4 mg, 0.2 mmol), anhydrous K₃PO₄ (42.4 mg, 0.2 mmol, 1 equiv) and anhydrous MeCN (1 mL) were added. The tube was capped, transferred out of the glove box and stirred at 100 °C for 20 hours, and then cooled down to room temperature. However, no product was detected via TLC.

4) Cu-Catalyzed decarboxylative iodination of 4,5-dimethoxy-2-nitrobenzoic acid 1 with NaI in the absence of Ag (entry 5, Table 2)

An oven-dried Schlenk tube equipped with a stir bar was charged with 4,5-dimethoxy-2-nitrobenzoic acid 1 (45.4 mg, 0.2 mmol), Cu(OAc)₂ (21.8 mg, 0.12 mmol, 0.6 equiv), NaI (45 mg, 0.3 mmol, 1.5 equiv) and 2,9-dimethyl-1,10-phenanthroline (12.5 mg, 0.06 mmol, 0.3 equiv). The tube was fitted with a rubber septum, and then it was evacuated and refilled with dioxygen three times. Under dioxygen, DMSO (4 mL) was added via syringe. The rubber septum was replaced with a Teflon screwcap under dioxygen flow, and the Schlenk tube was pressurized to 1 atm. With stirring, the reaction mixtures were heated at 160 °C for the indicated amount of time, and then cooled down to room temperature. The reaction mixtures were purified by flash column chromatography on silica gel (10% ether in hexane) to afford 24.1 mg (39%) of the product as a yellow solid.

5) Ag-Catalyzed decarboxylative iodination of 4,5-dimethoxy-2-nitrobenzoic acid 1 with NaI in the absence of Cu (entry 6, Table 2)

An oven-dried Schlenk tube equipped with a stir bar was charged with 4,5-dimethoxy-2-nitrobenzoic acid 1 (45.4 mg, 0.2 mmol), Ag₂SO₄ (6.2 mg, 0.02 mmol, 0.1 equiv), NaI (45 mg, 0.3 mmol, 1.5 equiv) and 2,9-dimethyl-1,10-phenanthroline (12.5 mg, 0.06 mmol, 0.3 equiv). The tube was fitted with a rubber septum, and then it was evacuated and refilled with dioxygen three times. Under dioxygen, DMSO (4 mL) was added via syringe. The rubber septum was replaced
with a Teflon screwcap under dioxygen flow, and the Schlenk tube was pressurized to 1 atm. With stirring, the reaction mixtures were heated at 160 °C for the indicated amount of time, and then cooled down to room temperature. However, no product was detected via thin layer chromatography (TLC).

6) The model reaction with radical scavenger (entries 7 and 8, Table 2)
An oven-dried Schlenk tube equipped with a stir bar was charged with 4,5-dimethoxy-2-nitrobenzoic acid 1 (45.4 mg, 0.2 mmol), Ag₂SO₄ (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc)₂ (21.8 mg, 0.12 mmol, 0.6 equiv), NaI (45 mg 0.3 mmol, 1.5 equiv), 2,9-dimethyl-1,10-phenanthrolineum (12.5 mg, 0.06 mmol, 0.3 equiv), TEMPO (62.5 mg, 0.4 mmol, 2.0 equiv) or BHT (88.1 mg, 0.4 mmol, 2.0 equiv). The tube was fitted with a rubber septum, and then it was evacuated and refilled with dioxygen three times. Under dioxygen, DMSO (4 mL) was added via syringe. The rubber septum was replaced with a Teflon screwcap under dioxygen flow, and the Schlenk tube was pressurized to 1 atm. With stirring, the reaction mixtures were heated at 160 °C for the indicated amount of time (unless otherwise specified), and then cooled down to room temperature. The resultant mixture was filtered through a short plug of silica gel and then concentrated in vacuo. The residue was then purified by flash chromatography on silica gel to provide the corresponding product 1a.
References
S22
S24
Agilent Technologies

Sample Name: S27
Sample Description: Agilent HPLC oven
Sample Directory: Chem/Comp/Agilent/Agilent
Sample Kind: Unknown
Sample ID: S27-0103-01
Sample Date: 2010-04-10
Sample Notes: n/a
Sample Measurements:
- Date: 2010-04-10
- Temperature: 25.0 °C / 77.0 °F
- Operation: n/a
- Retention: 500 mm
- Flow: 0.5 ml/min
- Column: 100 x 0.5 mm
- Conditions: LDI-TOF Mass Spectrometry
- Mass Range: 200-2000 Da
- Spectra: n/a
- Data Processing: n/a
- Instrument: n/a
- Date: 2010-04-10
- Total Time: 60 mins

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S51